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<b>(54) Title:</b> BIODEGRADABLE COMPOSITIONS COMPRISING STARCH DERIVATIVES  <b>(57) Abstract</b>  There is provided a biodegradable composition as obtained from a melt comprising a plasticizer and at least one member selected from alkenol homopolymers and/or alkenol copolymers which are combined under conditions sufficient to ensure uniform melt formation, characterized in that the composition includes a starch derivative. Said at least one member may be present in the composition at a concentration of from 10 to 200 parts per 100 parts of dry starch. The invention further relates to methods of making the composition, and to articles made from said composition.		

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- 1 -

Biodegradable compositions comprising starch derivatives

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The present invention relates to biodegradable polymer compositions capable of being formed by heat and pressure into articles having substantial dimensional stability. The invention relates particularly to biodegradable, 10 compositions comprising a starch derivative, a plasticizer and at least one member selected from alkenol homopolymers and/or alkenol copolymers which are combined under conditions sufficient to ensure uniform melt 15 formation. Such compositions are suitable for use, inter alia, in injection molding, in film formation, and in the formation of foamed packaging materials.

BACKGROUND TO THE INVENTION

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It is known that natural starch which is found in vegetable products can be treated at elevated temperatures to form a melt.

25

Such a melt may preferably be formed by heating the starch material above the glass transition and melting temperatures of its components so that such undergo endothermic rearrangement. Preferably the starch material contains a defined amount of water and melt 30 formation is carried out at an elevated temperature in a closed volume, and hence at an elevated pressure.

35

It is, however, possible to melt starch substantially in the absence of water, but in the presence of another suitable plasticizer, for example a liquid having a boiling point higher than the starch glass transition and melting temperature.

Different degrees of melt formation, which can be measured by various methods, are possible. One method, for example, is to microscopically determine the amount

- 2 -

of granular structure remaining in a starch melt. It is preferred that the starch is destructured, viz, that the melt is substantially uniform in character, that  
5 light microscopy at a magnification of about 500 X, indicates a substantial lack of, or reduction in, granular structure, that the starch so melted exhibits little or no birefringence and that x-ray studies indicate a substantial reduction in, or lack of, starch  
10 crystallinity in the melt.

It is an advantage of the present invention that compositions may be formed from starch which has a  
15 relatively low degree of destructureisation.

Ind. Eng. Chem. Prod. Res. Dev. (194; 23, page 594-595) describes the extrusion of starch extended water-soluble polyvinyl alcohol. According to this disclosure, the  
20 melt flow index of such an extrudate decreases with increasing starch concentrations so that a composition comprising a 1:1 ratio of a low molecular weight (20,000) polyvinyl alcohol and a low molecular weight (30,000) corn starch possesses a melt flow index of 0.53. A  
25 composition comprising such a low melt flow index is not suitable for the injection molding of articles therefrom, wherein a melt flow index of about 7 or higher is typically required. It is surprising that the present inventive compositions, which comprise relatively high  
30 concentrations of starch derivatives, can easily be injection molded.

The melt flow index of the composition is defined as the amount (in grams) of a thermoplastic material which can  
35 be forced in 10 minutes through a 2.0665mm orifice when subjected to a force of 0.2160 grams.

Moreover, it is implicit in the art of forming thermoplastics that the major components thereof should be of high molecular weight, and preferably that the

- 3 -

molecular weights of such components should be of similar magnitudes.

5 It is surprising that articles having excellent physical properties and dimensional stability can be formed from the present inventive compositions, wherein the polyvinyl alcohol, which has a low molecular weight in comparison  
10 with that of the starch derivative component of the composition, is present in high concentrations relative thereto.

#### SUMMARY OF THE INVENTION

15 According to the present invention, there is provided a biodegradable composition as obtained from a melt comprising a plasticizer and at least one member selected from alkenol homopolymers and/or alkenol copolymers which  
20 are combined under conditions sufficient to ensure uniform melt formation, characterized in that the composition includes a starch derivative.

By plasticizer is meant a substance which can be  
25 incorporated into a material to increase its flexibility, workability or distensibility or reduce the melt viscosity, lower the temperature of a second order transition, or lower the elastic modulus of the product. The term plasticizer includes solvent plasticizers and  
30 internal plasticizers.

The preferred plasticizer is water.

The starch derivative may be selected from the group  
35 consisting of starch esters and starch ethers, and the degree of substitution of said starch derivative may be from about 0.1 to about 3.0.

It is preferred that the degree of substitution of said derivative is at least 0.8, and more preferred that the degree of substitution is from about 0.8 to about 2.1.

- 4 -

In one embodiment of the composition, the starch derivative has an amylose content of up to about 95% by weight with respect to that of the starch derivative. It is preferred that the lower limit of the amylose content is between about 10 and about 15% by weight with respect to that of the starch derivative.

The starch derivative preferably has an equilibrium moisture content of less than about 7% at 25°C and a relative humidity of about 50%.

The at least one member may be present in the composition at a concentration of from 10 to 200 parts per 100 parts of dry starch derivative.

The alkenol homopolymer is preferably a polyvinyl alcohol which may be pre-plasticised with a polyhydric alcohol such as glycerol. The polyvinyl alcohol preferably is hydrolysed to an extent of from about 45 and about 100% and preferably has a number average molecular weight of about 15,000 to about 250,000, and more preferably has a number average molecular weight of from 15,000 to 150,000.

It is particularly preferred that the composition contains pre-treated polyvinyl alcohol in the form of a melt, obtained previously by adding sufficient energy to polyvinyl alcohol to melt it and substantially eliminate crystallinity in the melt. It is particularly preferred that the such crystallinity is substantially completely eliminated. Such pre-treatment of polyvinyl alcohol is disclosed in EP-A 0 415 357.

Alkenol copolymers as mentioned above are preferably synthetic copolymers containing vinyl alcohol units as well as aliphatic units as are obtained by copolymerization of vinyl esters, preferably vinyl acetate with monomers preferably ethylene, propylene,

- 5 -

isobutylene and/or styrene with subsequent hydrolysis of the vinyl ester group.

5 Such copolymers are known and are described in "Encyclopedia of Polymer Science and Technology, Interscience Publ. Vol. 14, 1971"

10 The composition may further comprise one or more compounds selected from the group of water-soluble and/or water-swellaable polymers and one or more hydrophobic thermoplastic polymer(s) which is/are substantially water-insoluble.

15 The composition may still further comprise at least one member selected from the group consisting of extenders, fillers, lubricants, mold release agents, other plasticisers, stabilisers, coloring agents, nucleating agents, flame retardants, boron-containing compounds and  
20 alkali and alkaline earth metal salts.

It will be appreciated that the concentration of the components in the composition, particularly the coloring  
25 agents, can be derived according to a Master-batching process, if desired.

The present invention further relates to compositions in the form of a melt comprising a plasticizer and at least  
30 one member selected from alkenol homopolymers and/or alkenol copolymers which are combined under conditions sufficient to ensure uniform melt formation, characterized in that the composition includes a starch derivative.

35 The present invention still further relates to shaped articles, including a granulate or pellet, made from said composition or melt.

The melted compositions may be further processed into shaped articles by a process selected from the group

- 6 -

consisting of: injection molding, compression molding,  
filming, blow molding, vacuum forming, thermoforming,  
extrusion, co-extrusion, foaming, and combinations  
5 thereof.

The present invention further relates a method for  
producing the composition of the present invention,  
characterized by:  
10

a) providing a starting composition comprising a starch  
derivative, a plasticizer and at least one member  
selected from alkenol homopolymers and/or alkenol  
15 copolymers;

b) adjusting the plasticizer content of the composition  
to between about 0.5 and about 40% by weight of the total  
composition during processing or plastification;

20 c) heating the thereby adjusted composition in a  
closed volume at a temperature of between 100 and 220°C  
and at a pressure corresponding at least to the moisture  
vapor pressure at said temperature for a time at least  
25 sufficient to form a melt of the composition;

d) removing any excess moisture before the extruder die  
to obtain a moisture content of between about 5% and  
about 20%;

30 and -

e) extruding the thereby heated composition.

The present invention further includes a melt as obtained  
35 according to the method.

The invention will be further apparent from the following  
description, in conjunction with the following examples  
and the appended claims.



- 7 -

SPECIFIC DESCRIPTION

The present invention is defined by the appended claims.  
5 In particular, the invention provides a biodegradable composition as obtained from a melt comprising a plasticizer and at least one member selected from alkenol homopolymers and/or alkenol copolymers which are combined  
10 under conditions sufficient to ensure uniform melt formation, characterized in that the composition includes a starch derivative.

The melt preferably is thermoplastic in character.

15 Said derivative is made according to known methods from at least one member selected from the group consisting of starches of vegetable origin, which starches are obtained from potatoes, rice, tapioca, corn, pea, rye, oats and  
20 wheat.

The starch derivative may be selected from the group consisting of starch esters and starch ethers, and may have a degree of substitution of from about 0.1 to about  
25 3.0.

It is preferred that the degree of substitution of said derivative is at least 0.8, and more preferred that the degree of substitution is from about 0.8 to about 2.1.

30 The derivative may be a starch ester selected from the group consisting of acetates, propionates, butyrates and the starch esters of C5 to C12 fatty acids.

35 Where the derivative is a starch acetate the degree of substitution is from about 0.5 to about 1.8, more preferably the starch is substituted to a degree of from about 0.7 to about 1.8, and most preferably the degree of substitution is from about 0.8 to about 1.5.

- 8 -

Where the derivative is a starch propionate, the degree of substitution is from about 0.5 to about 1.6, and more preferably is from about 0.7 to about 1.4.

The derivative may be selected from the group consisting of alkyl ethers and hydroxyalkyl ethers, hydroxyalkylalkylethers and mixtures thereof.

Preferred starch ethers include the methyl ether, ethylether, propylether, butylether, hydroxymethylether, hydroxyethylether, hydroxypropylether, hydroxyethylmethylether and hydroxypropylmethylether and derivatives thereof.

In one embodiment of the composition, the starch derivative has an amylose content of up to about 95% by weight with respect to that of the starch.

In another embodiment of the composition, the derivative has an amylose content of up to about 85% by weight with respect to that of the starch.

In a further embodiment of the composition, the derivative has an amylose content of up to about 75% by weight with respect to that of the starch.

In a still further embodiment of the composition, the derivative has an amylose content of up to about 65% by weight with respect to that of the starch.

In a still further embodiment of the composition, the derivative has an amylose content of up to about 45% by weight with respect to that of the starch.

In a still further embodiment of the composition, the derivative has an amylose content of between about 30 and about 35% by weight with respect to that of the starch.

- 9 -

It is preferred that the lower limit of the amylose content is between about 10 and about 15% by weight with respect to that of the starch.

The starch derivative may have an equilibrium moisture content of less than about 7% at 25°C and a relative humidity of about 50%, and more preferably has an equilibrium moisture content of less than about 5% at 25°C and a relative humidity of about 50%.

The at least one member may be present in the composition at a concentration of from 10 to 200 parts per 100 parts of dry starch.

The composition may comprise from about 10 to about 120 parts of said polymer and / or copolymer per 100 parts by weight of dry starch derivative, and in a preferred embodiment, the composition comprises from about 10 to about 100 parts of said polymer or copolymer per 100 parts of starch derivative.

The composition may also comprise a polymer or copolymer content of from 10 to 65 parts, and particularly from 20 to 40 parts with respect to 100 parts of starch derivative.

The alkenol homopolymer is preferably polyvinyl alcohol (PVA) having a number average molecular weight of at least about 15,000 (which corresponds to a degree of polymerization of at least 340). It is more preferred that the PVA has a number average molecular weight of between about 50,000 and 250,000, and most preferred that it has a number average molecular weight of about 80,000 to 120,000. Where the composition is foamed it is preferred that the number average molecular weight of the polyvinyl alcohol is between about 160,000 and 250,000 and more preferably between 160,000 and 200,000.

- 10 -

Polyvinyl alcohol (PVA) is generally made from hydrolysis, or alcoholysis of polyvinyl acetate. The degree of hydrolysis to provide a polyvinyl alcohol for  
5 use in the present invention preferably is from about 75 to about 99.9 mole %, and more preferably is from about 80 to 99.9 mol %. It is most preferred that the degree of hydrolysis is from about 87 to 99.9 mol%.

10 Such polyvinyl alcohols are known and are sold, by Air Products And Chemicals Inc, of 7201 Hamilton Boulevard, Allentown, USA, under the name of Airvol 540S (degree of hydrolysis 87-89%, molecular weight about 106 -110, 000);  
15 Airvol 205S (degree of hydrolysis 87-89%, molecular weight about 110 - 31,000), Elvanol 90-50 (degree of hydrolysis 99.0 to 99.8%, molecular weight about 35 to about 80,000) and Airvol 107 (degree of hydrolysis 98.0 to 98.8%, molecular weight 11,000 to 31,000).

20 EP-A 0 415 357 in the name of Air Products and Chemicals Inc, describes extrudable polyvinyl alcohol compositions, and methods for their preparation. The method according to EP-A 0 415 357 comprises adding sufficient energy to  
25 the polyvinyl alcohol to both melt it and essentially eliminate the crystallinity in the melt whilst simultaneously removing energy from the melt at a rate sufficient to avoid decomposition of the polyvinyl alcohol.

30 Accordingly, the present invention contemplates the use in the present inventive compositions of polyvinyl alcohol pre-treated according to the disclosure of EP-A 0 415 357. Thus the present inventive composition contains  
35 pre-treated polyvinyl alcohol in the form of a melt which has been obtained previously by adding sufficient energy to polyvinyl alcohol to both melt it and substantially eliminate crystallinity in the melt, whilst simultaneously removing energy from the polyvinyl alcohol melt at a rate sufficient to avoid its decomposition.

- 11 -

The pre-treated polyvinyl alcohol may be plasticised by the addition thereto of a polyhydric alcohol plasticizer in an amount of from 2 to 30% by weight of the polyvinyl alcohol. It is preferred that the pre-treated polyvinyl alcohol is plasticised by the addition thereto of a polyhydric alcohol plasticizer in an amount of from 2 to 20% by weight of the polyvinyl alcohol. The pre-treated polyvinyl alcohol may further comprise sodium acetate and phosphoric acid in a molar ratio of about 2 to 1. The sodium acetate is present in the polyvinyl alcohol as a by product of its method of production and under the conditions of melt formation such sodium acetate acts as a catalyst for decomposition of the polyvinyl alcohol. Accordingly, phosphoric acid may be added to the polyvinyl alcohol composition from which the pre-treated polyvinyl alcohol melt is made, in the ratio of 1 mole of acid per 2 moles of acetate, in order to neutralize said sodium acetate. Low ash polyvinyl alcohol, which is essentially free of sodium acetate, does not require the addition of such phosphoric acid.

The pre-treated melt of polyvinyl alcohol has a maximum melt temperature, as determined by differential scanning calorimetry, which is at least about 5°C lower than that of the corresponding untreated polyvinyl alcohol, preferably at least about 10°C lower than that of the untreated polyvinyl alcohol, and particularly preferably at least about 15°C lower than that of the untreated polyvinyl alcohol.

The formation of such a pre-treated melt of polyvinyl alcohol requires the input of at least about 0.27kWh/kg of specific energy to the polyvinyl alcohol, and typically requires from about 0.3 to about 0.6kWh/kg of such energy.

The upper practical limit of energy input would be about 0.6kWh/kg because any energy beyond that necessary to melt the polyvinyl alcohol and eliminate crystallinity

- 12 -

must be removed as "waste energy" reducing the efficiency of the formation of the pre-treated polyvinyl alcohol.

5 Optimally the polyvinyl alcohol requires an input of about 0.35 to about 0.45kWh/kg both to melt it and substantially eliminate crystallinity in the melt.

10 Said alkenol copolymers may contain vinyl alcohol units and aliphatic chain units and may be as obtained by co-polymerization of vinyl acetate with ethylene and/or propylene, preferably with ethylene and subsequent hydrolysis of the vinyl acetate group. Such copolymers  
15 may have differing degrees of hydrolysis.

Preferred are ethylene/vinyl alcohol polymers (EVOH) and propylene/vinyl alcohol polymers. Most preferred are the ethylene/vinyl alcohol polymers. The molar ratio of vinyl  
20 alcohol units to alkylene units is preferably from about 40 : 60 to about 90 : 10 and more preferably from about 45 : 55 to about 70 : 30. The most preferred EVOH has an ethylene content of 44%.

25 The starch derivative which is present in the composition is at least one member selected from the group consisting of chemically modified starches of vegetable origin, which starches are obtained from potatoes, rice, tapioca, corn, pea, rye, oats, wheat, including physically  
30 modified starch, irradiated starch, starch in which mono or divalent ions associated with phosphate groups therein have been removed, either partly or wholly, and optionally replaced, either partly or wholly, by different divalent ions or with mono or polyvalent ions;  
35 pre-extruded starches and starches which have been so heated as to undergo the specific endothermic transition characteristically preceding oxidative and thermal degradation.

The starch component of the composition according to the invention includes starch melted in the absence of added

- 13 -

water, but in the presence of another plasticizer - such as glycerol.

5 The preferred plasticizer is, however, water.

10 Preferably the starch is formed into a melt in the presence of water which may be present in the starting composition, from which the composition of the present invention is made, at between about 0.5 and about 40% by weight, based on the total weight of the starting composition.

15 The composition according to the invention may thus have a water content of between about 10 and about 20% by weight, and preferably of between about 14 and about 18% by weight, and particularly of about 17% by weight, based on the weight of the composition as explained herein.

20 The starch derivative may be mixed with the polymer or copolymer and optionally other additives as mentioned hereinbelow in any desired sequence. For example, the derivative may be mixed with all of the intended  
25 additives, including polymer or copolymer to form a blend, which blend may then be heated to form a uniform melt which will, in general, be thermoplastic.

The starch derivative may, however, be mixed with  
30 optional additives, the derivative melted and granulated before addition of the polymer or copolymer, for example the polyvinyl alcohol, which mix may then be further processed.

35 Preferably, however, the derivative is mixed with additives together with the polymer or copolymer, for example polyvinyl alcohol, to form a free flowing powder, which is useful for continuous processing, and melted and either granulated or extruded directly into the solidified composition of the present invention.

- 14 -

- The composition may optionally consist at least of the combination of a starch derivative and one member selected from alkenol homopolymers and copolymers which have been pre-processed. Such pre-processing may involve the provision of granulates or pellets which have been manufactured under conditions sufficient to have obtained uniform melt formation of the components.
- Alternatively, and or additionally, the alkenol homopolymers and copolymers may have been pre-plasticised with, for example, a polyhydric alcohol such as glycerol.
- The starch derivative present in the composition may have been pre-melted in the presence of from 15 to 40% moisture, by weight thereof, and at a temperature and pressure within the ranges as given above.
- Optionally the composition comprises at least one member selected from the group consisting of extenders, fillers, lubricants, mould release agents, plasticisers, stabilisers, coloring agents, and flame retardants.
- The composition may further contain in an amount up to 60 %, preferably in an amount up to 35% and most preferably in an amount up to 25% by weight of the total composition, one or more hydrophobic thermoplastic polymer(s) which is/are substantially water-insoluble.
- Such a polymer is one that dissolves water at a rate of less than 25 grams per 100 grams of the dry polymer, and more preferably at a rate of less than 15 grams per 100 grams of dry polymer when immersed in water at room temperature. Examples of hydrophobic thermoplastic polymers are polyolefines, such as polyethylene (PE), polyisobutylenes, polypropylenes, vinylpolymers such as poly(vinyl chloride) (PVC), poly(vinyl acetates), polystyrenes; polyacrylonitriles (PAN); polyvinylcarbazoles (PVK); substantially water-insoluble poly(acrylic acid) esters or poly(methacrylic acid) esters; polyacetals (POM); polycondensates such as



- 15 -

- polyamides (PA), thermoplastic polyesters, polycarbonates, polyurethanes, poly(alkylene terephthalates); polyarylethers; thermoplastic polyimides; but also  
5 poly(hydroxybutyrate) (PHB) and high molar-mass, substantially water-insoluble poly(alkylene oxides) such as polymers of ethylene oxide and propylene oxide as well as their copolymers are included.
- 10 Further included are hydrophobic thermoplastic copolymers of the different kinds known such as ethylene/vinyl acetate-copolymers (EVA); ethylene/vinyl alcohol-copolymers (EVOH); ethylene/acrylic acid-copolymers (EAA); ethylene/ethyl acrylate-copolymers  
15 (EEA); ethylene/methyl acrylate-copolymers (EMA); ABS - copolymers; styrene/acrylonitrile-copolymers (SAN); and mixtures thereof.
- 20 The extenders include water-soluble an/or water-swellaable polymers including known thermoplastic polymers such as gelatin, vegetable gelatins, acrylated proteins; water-soluble polysaccharides such as: alkylcelluloses, hydroxyalkylcelluloses and hydroxyalkylalkylcelluloses,  
25 such as: methylcellulose, hydroxymethylcellulose, hydroxyethylcellulose, hydroxypropylcellulose, hydroxyethylmethylcellulose, hydroxypropylmethylcellulose, hydroxybutylmethylcellulose, cellulose esters and  
30 hydroxyalkylcellulose esters such as: cellulose acetylphthalate (CAP), Hydroxypropylmethyl-cellulose (HPMCP); carboxyalkylcelluloses, carboxyalkyl-alkylcelluloses, carboxyalkylcellulose esters such as: carboxymethylcellulose and their  
35 alkali-metal salts; the analogous derivatives of starch as named for all the cellulose derivatives above; water-soluble synthetic polymers such as: poly(acrylic acids) and their salts and essentially water soluble poly(acrylic acid) esters, poly(methacrylic acids) and their salts and essentially water-soluble poly(methacrylic acid) esters, essentially water soluble

- 16 -

poly(vinyl acetates), poly(vinyl acetate phthalates) (PVAP), poly(vinyl pyrrolidone), poly(crotonic acids); cationically modified acrylates and methacrylates  
5 possessing, for example, a tertiary or quaternary amino group, such as the diethylaminoethyl group, which may be quaternized if desired; and mixtures of such polymers.

10 By the term "water-soluble or water-swellaable polymer" is meant a polymer which absorbs or adsorbs at least 30% of water by weight with respect to that of the dry polymer when such is immersed in liquid water at room  
15 temperature.

Suitable fillers include, for example, wood-derived materials, and oxides of magnesium, aluminum, silicon, and titanium. The fillers are present in the composition  
20 at a concentration of up to about 20% by weight, and preferably between about 3.0 and about 10%, by weight, based on the total weight of the composition.

The lubricants include stearates of aluminum, calcium,  
25 magnesium, and tin, as well as the free acid and magnesium silicate, silicones and substances such lecithin, and mono and diglycerides, which - for the purpose of the present invention -

function in like-manner. Suitable lubricants further  
30 include unsaturated fatty acid amides, preferably amides of C 18 - C 24 unsaturated fatty acids, such as the amide of cis-13-docosenoic acid (erucamide) and amides of C 12 - C 24 carboxylic acids, such as the amide of docosanoic acid (behenamide). The particularly preferred lubricant  
35 is stearic acid, which is present in the composition in an amount of up to 10 parts per 100 parts of starch derivative, preferably in an amount of from 1 to 3 parts per 100 parts of derivative, and most preferably is present in the composition in an amount of 1 part per 100 parts of derivative.

- 17 -

The composition of the present invention may also comprise a nucleating agent, - particularly so where the composition is in foamed form - having a particle size of  
5 from 0.01 to 5 microns, selected from the group consisting of silica, titania, alumina, barium oxide, magnesium oxide, sodium chloride, potassium bromide, magnesium phosphate, barium sulphate, aluminum sulphate,  
10 boron nitrate and magnesium silicate, or mixtures thereof. It is preferred that said nucleating agent is selected from amongst silica, titania, alumina, barium oxide, magnesium oxide, sodium chloride, and magnesium silicate, or mixtures thereof.

15 The particularly preferred nucleating agent is magnesium silicate (micro talcum), which is present in the composition in an amount of up to 10 parts of agent per 100 parts of derivative. Preferably the agent is present  
20 in the composition in an amount of from 1 to 3 parts per 100 parts of derivative, and most preferably in an amount of 2 parts per 100 parts of derivative.

Plasticisers include urea and low molecular weight  
25 poly(alkylene oxides), such as, for example, poly(ethylene glycols), poly(propylene glycols) poly(ethylene-propylene glycols), organic plasticisers of low molecular mass, such as, for example, glycerol; pentaerythritol; glycerol monoacetate, diacetate, or  
30 triacetate; propylene glycol; sorbitol; sodium diethylsulfosuccinate; triethyl citrate and tributyl citrate and other substances which function in like manner.

35 Such plasticisers are preferably present in the composition at a concentration of between about 0.5% and about 40% by weight, and more preferably between about 0.5% and about 5% by weight, based on the weight of all of the components, including the water therein.

- 18 -

Preferably the sum of the plasticizer (including water where such is present as a plasticizer) content of the composition does not exceed about 25% by weight, and most preferably does not exceed about 20% by weight, based on the total weight of the composition.

Stabilisers include anti-oxidants such as thiobisphenols, alkylidenbisphenols, secondary aromatic amines; stabilisers against photo-decomposition, such as, for example, uv absorbers and quenchers; hydroperoxide decomposers; free radical scavengers, and anti-microbial agents.

Coloring agents include known azo dyes, organic or inorganic pigments, or coloring agents of natural origin. Inorganic pigments are preferred, such as the oxides of iron or titanium, these oxides being present in the composition at a concentration of between about 0.01 and about 10% by weight, and preferably present at a concentration of between about 0.05 and about 3% by weight, based on the total weight of the composition. Most preferably the coloring agents are present in the composition in an amount of about 0.03 to about 0.07% by weight with respect to the total composition. Iron oxide in an amount of 0.05% by weight with respect to that of the 0.05%.

The composition may further comprise flame retardants which, for example, comprise phosphorous, sulphur and halogens, or mixtures thereof.

Suitable phosphorous-containing flame retardants include diethyl-N,N-bis(2-hydroxyethyl) aminomethyl phosphonate; dimethyl methylphosphonate; phosphonic acid, methyl-, dimethylester, polymer with oxirane and phosphorous oxide; aliphatic phosphate/phosphonate oligomers; tributyl phosphate; triphenyl phosphate; tricresyl phosphate; 2-ethylhexyl diphenyl phosphate; and tributoxyethyl phosphate. These retardants are available

- 19 -

from Akzo Chemicals Inc. of 300 South Riverside Plaza, Chicago, Illinois, USA.

- 5 Further suitable phosphorous-containing retardants include: bis (hydroxypropyl) sec.butyl phosphine oxide which can be obtained from the Chemical Products Group of FMC Corporation, 2000 Market Street, Philadelphia, Pennsylvania 19103, USA; and the following compounds  
10 obtainable from Albright and Wilson, Americas Inc, of P.O. Box 26229, Richmond, Virginia, 23260, USA: polypropoxylated dibutyl pyrophosphoric acid; a mixture of  
15 methyl-, (5-ethyl-2-methyl-1,3,2-dioxaphosphorinan-5-yl)methyl ethyl ester, P-oxide and phosphonic acid, methyl-, bis [(5-ethyl-2-methyl-1,3,2-dioxaphosphorinan-5-yl)methyl] ester, P,P'-dioxide as sold under the trade name Amgard V19;  
20 ammonium polyphosphate; ethylenediamine polyphosphate; melamine phosphate; dimelamine phosphate; and microencapsulated red phosphorous.

- Where ammonium polyphosphate and ethylenediamine  
25 polyphosphate are used as flame retardants, it is preferred that they are buffered with disodium orthophosphate so that they are thereby less corrosive to the equipment used for processing the composition comprising them.

- 30 A still further suitable phosphorous containing flame retardant is guanidinium phosphate which can be obtained from Chemie Linz GmbH of St Peter Strasse 25, A-4021, Linz, Austria.

- 35 Suitable halogen-containing flame retardants include chlorinated paraffin, which is obtainable from Occidental Chemical Corporation, of 360 Rainbow Boulevard South, Box 728, Niagra Falls, New York 14302; tetrabromo phthalic anhydride, and penta-, octa- and decabromo diphenyl oxide, which are obtainable from Great Lakes Chemical

- 20 -

Corporation, of P.O. Box 2200, West Lafayette, Indiana, 47906, USA; and bromochlorinated paraffin, brominated epoxy resin, brominated polystyrene, tris (2-chloropropyl) phosphate and tetrakis hydroxymethyl phosphonium chloride which may be obtained from Albright and Wilson at the address given above.

Further suitable halogen-containing compounds include dibromo neopentyl glycol and tribromo neopentyl alcohol which are obtainable from AmeriBrom Inc of 1250 Broadway New York, New York 10001, USA.

Suitable sulphur containing-retardants include ammonium sulfate; ammonium sulfamate; and tetrakis (hydroxymethyl) phosphonium sulfate; all of which may be obtained from the American Cyanamid Company, of One Cyanamid Plaza, Wayne, New Jersey, 07470, USA. Guanidinium sulfate, obtainable from Chemie Linz at the address given above, may also be used as a flame retardant.

The above mentioned flame retardants are present in the starch-containing composition in an amount of from 0.1 to 10%, preferably from 1 to 6%, and most preferably from 2 to 4%, all percentages being by weight with respect to that of the derivative component of the composition.

Other suitable flame retardants which may be present in the composition of the present invention include aluminum trihydrate; aluminum acetylacetonate; aluminum acetate; sodium aluminum hydroxy carbonate; magnesium aluminum hydroxy carbonate; antimony oxide; molybdic oxide; ammonium octamolybdate; zinc molybdate; magnesium hydroxide; zinc borate; ammonium pentaborate; boric acid; and sodium tetraborate. These flame retardants are generally available, and the Borax compounds in particular may be obtained from the United States Borax and Chemical Corporation, of 3075 Wilshire Boulevard, Los Angeles, California 90010, USA.

- 21 -

These latter flame retardants may be present in the composition in an amount of from 1 to 90% by weight with respect to the starch derivative component of the composition, and preferably are present in the composition in an amount of from 20 to 80% and most preferably from 40 to 75%.

10 The particularly preferred flame retardants are guanidinium phosphate, ammonium polyphosphate and/or ethylenediamine polyphosphate (in the presence or absence of disodium orthophosphate), and guanidinium sulphate or ammonium sulphate.

13 Still further substances which may be added to the composition include animal or vegetable fats, preferably in their hydrogenated forms, especially those which are solid at room temperature. Such fats preferably have a melting point of at least 50°C and include triglycerides of C12-, C14-, C16- and C18- fatty acids.

23 The fats are added to the material comprising the thermoplastic melt alone without extenders or plasticisers, or to the melt together with mono- or diglycerides or phosphatides, of which lecithin is preferred. Said mono- and diglycerides are preferably derived from said animal or vegetable fats.

30 The total concentration of said fats, mono-, diglycerides and phosphatides may be up to 5% by weight, based on the total weight of the composition.

33 Still further compounds which may be added to, or present in the composition include boron-containing compounds, particularly so when the composition is formed into films, sheets or fibers. The presence of such compounds in the composition yields articles which have improved transparency, Young's modulus and tear strength. The preferred boron-containing compounds are boric acid, metaboric acid, alkali and alkaline earth metal salts,

- 22 -

borax and derivatives thereof. Said compounds may be present in the composition in an amount of between 0.002 and 0.4%, by weight with respect to that of the composition, and preferably are present at a concentration of between about 0.01 and 0.3%, likewise by weight.

Inorganic salts of alkali or alkaline earth metals, particularly LiCl and NaCl may be additionally present in the composition in an amount of between 0.1 and 5% by weight with respect to that of the total composition. The presence of such salts in the composition still further improves the Young's modulus, transparency and tear strength of articles made from the composition.

It will be appreciated that the concentration of the components, particularly the coloring agents and borax containing compounds, in the composition can be derived according to a Master-batching process, if desired.

The compositions described herein above form thermoplastic melts on heating under conditions of controlled temperature and pressure. Insofar as such melts may be processed by any conventional shaping process the present invention also refers to such processes when used to shape the composition or melt of the present invention. Thus such melts can be processed in the manner used for conventional thermoplastic materials, such as injection molding, blow molding, extrusion, coextrusion, compression molding, vacuum forming, and thermoforming to produce shaped articles. Whilst such articles include containers, cartons, trays, cups (particularly for candles where the composition comprises a flame retardant), dishes, sheets, and packaging materials, including the loose fill variety, the shaped articles also include pellets and granulates which may be ground to make powders for use in the manufacture of shaped articles. Particularly preferred



- 23 -

articles are in foamed form, in injection molded form or are in extruded form.

- 5 The range of pressures and temperatures suitable for injection molding, filming, foaming and extrusion molding are as disclosed hereinbelow.

10 Injection molding of the composition

In order to melt the starch according to the invention, it is heated at a sufficient temperature for a time sufficient to enable uniform melt formation.

- 15 The composition is preferably heated in a closed volume, such as a closed vessel, or in the finite volume created by the sealing action of unmolten feed material, which action is apparent in the screw and barrel of an extruder or injection molding equipment.

- 20 Thus said screw and barrel is to be understood as a closed volume. Pressures created in such a volume correspond to the vapor pressure of the plasticizer (usually water) at the used temperature. It will be appreciated that pressures may be applied or generated, as is known to be possible in the use of said screw and barrel.

- 30 The preferred applied and/or generated pressures are in the range of pressures which occur in injection molding or extrusion are known per se, being up to about  $150 \times 10^5 \text{ N/m}^2$ , preferably up to about  $75 \times 10^5 \text{ N/m}^2$  and most preferably up to about  $50 \times 10^5 \text{ N/m}^2$ .

- 35 The temperature used in injection molding of the composition is preferably within the range of  $100^\circ\text{C}$  to  $220^\circ\text{C}$ , more preferably within the range of from  $160$  to  $200^\circ\text{C}$ , and most preferably within the range of  $160$  to  $180^\circ\text{C}$ , the precise temperature being dependent up on the type and nature of the derivative used. In terms of

- 24 -

ease of processing it is preferred that potato or corn starch derivative is used.

5 The thus obtained melted composition is granulated and is ready to be mixed with further components according to a chosen mixing and processing procedure to obtain a granular mixture of melted starch starting material to be fed to the screw barrel.

10

#### Filming of the composition

The composition is plasticised as above, except that preferably it is heated to a temperature typically about 10 to about 20°C higher than those routinely used during  
15 injection molding and extrusion of the composition.

#### Foaming of the Composition

20 The process for forming the composition of the present invention into foams comprises:

a) providing a starting composition comprising a starch derivative, plasticizer and at least one member selected  
25 from alkenol homopolymers and/or alkenol copolymers;

b) adjusting the plasticizer content of the composition to between about 15 and about 40% by weight of the total composition during processing or plastification;

30

c) heating the thereby adjusted composition at a temperature of between 100 and 220°C and for a time at least sufficient to form a uniform melt of the composition;

35

d) removing any excess moisture before the extruder die to obtain a moisture content of between about 10% and about 20%; and -

e) extruding the thereby heated composition under conditions whereby the extrudate assumes a cross section

- 25 -

greater than that of the exit orifice of the extruder die.

5

It is preferred that the plasticizer is water and that, prior to extrusion, the moisture content of the composition is adjusted to between 14 and 20%, more preferably between 16 and 18% and most preferably to 17%  
10 by weight of the total composition, and that the composition is heated at a temperature of from about 160°C to about 200°C and most preferably from about 180°C to about 200°C, and at a pressure corresponding at least to the moisture vapor pressure at said temperature for a  
15 time of at least 30 seconds.

The composition may be molded subsequent to its extrusion using known thermoforming processes.

20

The invention will be further apparent from a consideration of the following Examples.

#### Example 1

25

This Example describes the injection molding of candle cups from an extruded blend of polyvinyl alcohol and a starch derivative.

- 30 A mixture of hydroxy propylated maize starch or hydroxy-propylated high amylose starch (Hylon VII and hydroxypropylated Hylon VII respectively, obtainable from National Starch and Chemical Corporation of Funderne Avenue P.O. Box 6500 Bridgewater, New Jersey 08807 USA),  
35 Boeson VP (as sold by Boehringer Ingelheim), and lecithin (as sold as Metarin P by Lucas Meyer) present in the ratio of 100: 2: 1 respectively is prepared.

13.6 kg of this mixture is fed into the entry port of a twin screw extruder (Leistritz model LSM 34) having screws co-rotating in a horizontal cylindrical barrel and

- 26 -

an outlet die mounted at the discharge end of the extruder, opposite its entry port.

5 To this mixture is added 440 grams of glycerol, 5.2 kg of pre-plasticised polyvinyl alcohol having a number average molecular weight of about 15,000 to 45,000 and a degree of hydrolysis of 88 to 99%, and sufficient water to enable the combined mixture to be compounded  
10 appropriately. The amount of water added is dictated to a large extent by the nature of the derivative and is easily determined by the skilled man.

15 The composition is then heated to a temperature of about 175°C for about 30 to 120 seconds at a suitable pressure necessary to avoid the formation of water vapor at said temperature.

20 Ammonium sulphate is dissolved in water and added to the heated and pressurized starch composition prior to extrusion of the composition from the outlet die of the extruder.

25 The ammonium sulphate is added in such an amount that its final concentration in the cooled extrudate is 3.5% by weight with respect to that of the starch derivative component thereof.

30 The thus melted composition is extruded from the outlet die of the extruder, and the extrudate cooled and pelletized.

The pellets of the pre-blended mixture as obtained above  
35 (H<sub>2</sub>O content preferably about 11%) are fed through a hopper to an injection molding machine (Arburg 320) fitted with a mould suitable for the production of candle cups.

The candle cups so produced have excellent physical properties, substantial dimensional stability and are

- 27 -

made from a composition which is sufficiently flame retarded to meet the DIN 75200 flame retardancy standards.

5

### Example 2

Example 1 is repeated except that the composition from which the candle cups are made is altered. The altered  
10 composition comprises hydroxy-propylated Hylon VII, obtainable from National Starch and Chemical Corporation of Funderne Avenue P.O. Box 6500 Bridgewater, New Jersey 08807 USA), Boeson VP (as sold by Boehringer Ingelheim),  
15 and lecithin (as sold as Metarin P by Lucas Meyer) present in the ratio of 100: 2: 1 respectively.

10 kg of this mixture is fed into the entry port of a twin screw extruder (Leistritz model LSM 34) having  
20 screws co-rotating in a horizontal cylindrical barrel and an outlet die mounted at the discharge end of the extruder, opposite its entry port.

To this mixture is added 440 grams of glycerol, 3 kg of  
25 polyvinyl alcohol having a number average molecular weight of about 11,000 to 31,000 and a degree of hydrolysis of 98 to 98.8%, and sufficient water to enable the combined mixture to be compounded appropriately.

30 The starch composition is then melted at a pressure (about 1200 bar) necessary to avoid the formation of water vapor at the temperature at which the composition is melted.

35 Ammonium sulphate is dissolved in water and added to the heated and pressurized composition prior to extrusion of the composition from the outlet die of the extruder.

The ammonium sulphate is added in such an amount that its final concentration in the cooled extrudate is 3.5% by

- 28 -

weight with respect to that of the starch derivative component thereof.

<sup>5</sup> The thus melted starch is extruded from the outlet die of the extruder, and the extrudate cooled and pelletized.

The pellets of the pre-blended mixture as obtained above (H<sub>2</sub>O content preferably about 11%) are fed through a  
<sup>10</sup> hopper to an injection molding machine (Arburg 320) fitted with a mould suitable for the production of candle cups.

<sup>15</sup> The candle cups so produced have excellent physical properties, substantial dimensional stability and are made from a composition which is sufficiently flame retarded to meet the DIN 75200 flame retardancy standards.

<sup>20</sup> Example 3

Example 1 is repeated except that the flame retardant used is ethylenediamine polyphosphate, present in the  
<sup>25</sup> composition in an amount of 4% by weight with respect to that of the starch derivative component thereof.

In Examples 1 to 3, the flame retardant is added at a late stage in the compounding of the composition prior to  
<sup>30</sup> its injection molding, and the residence of the composition (now comprising the flame retardant) in the extruder is kept to a minimum.

In addition, that part of the extruder which contacts the  
<sup>35</sup> flame retarded starch composition may be especially adapted to reduce the corrosive effects of the retardant on the extruder.

Example 4

10kg of corn starch acetate having a degree of

- 29 -

substitution of about .8, 2kg of polyvinyl alcohol having a number average molecular weight of about 106,000 to 110,000 and degree of hydrolysis of between 87 and 89%,  
5 (Airvoll 540S), 200g of magnesium silicate and 100g of stearic acid are combined. The moisture content of the combined components is then adjusted to between 25 to 30% by weight with respect to the moistened starch mix.

10 The thus adjusted starch is fed into the entry port of a twin screw extruder (Leistritz model LSM 34) having screws co-rotating in a horizontal cylindrical barrel and an outlet die mounted at the discharge end of the extruder, opposite its entry port.  
15

The starch composition is then heated to a temperature of 170°C for about 70 seconds at a suitable pressure necessary to avoid the formation of water vapor at said temperature.  
20

The thus melted starch is extruded from the outlet die of the extruder, and the extrudate cooled and pelletized.

25 The pelletized melted starch mix is conditioned to a moisture content of about 17%, and then fed into the entry port of a single screw extruder having a screw length to diameter ratio of in the range of 25. Extruders having a ratio of from 10 to 30 are also  
30 useable in the process according to the present invention.

The thus formed mix is heated to 190°C for from 20-60 seconds and then extruded. Upon emerging from the exit  
35 orifice of the extruder die, the extrudate assumes a cross section greater than that of the said orifice to form a foam material suitable for use as a packaging material. Open and closed cell foams are thus produced which have excellent properties with respect to density, resilience and compressibility.

- 30 -

It will be appreciated that it is not intended to limit the invention to the above examples only, many variations thereto and modifications thereof being possible to one  
5 skilled in the art without departing from its scope, which is defined by the appended claims.

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- 31 -

## WHAT WE CLAIM IS:

1. A composition as obtained from a melt comprising a plasticizer and at least one member selected from alkenol homopolymers and/or alkenol copolymers which are combined under conditions sufficient to ensure uniform melt formation, characterized in that the composition includes a starch derivative.
2. A composition according to claim 1, in which the starch derivative is selected from the group consisting of starch esters and starch ethers.
3. A composition according to claim 2, in which the degree of substitution of said starch derivative is from about 0.1 to about 3.0.
4. A composition according to claim 3, in which the degree of substitution of said derivative is at least 0.8.
5. A composition according to claim 4, in which the degree of substitution is from about 0.8 to about 2.1.
6. A composition according to claim 3, in which the derivative is a starch ester selected from the group consisting of acetates, propionates, butyrates and the starch esters of C5 to C12 fatty acids.
7. A composition according to claim 6, in which the derivative is a starch acetate having a degree of substitution of from about 0.5 to about 1.8.
8. A composition according to the preceding claim, in which the derivative is a starch acetate having a degree of substitution of from about 0.7 to about 1.8.
9. A composition according to the preceding claim, in which the derivative is a starch acetate having a degree of substitution of from about 0.8 to about 1.5.

- 32 -

10. A composition according to claim 6, in which the derivative is a starch propionate having a degree of substitution of from about 0.5 to about 1.6.

11. A composition according to the preceding claim, in which the derivative is a starch propionate having a degree of substitution of from about 0.7 to about 1.4.

10

12. A composition according to claim 3, in which the derivative is selected from the group consisting of alkyl ethers and hydroxyalkyl ethers, hydroxyalkylalkylethers and mixtures thereof.

15

13. A composition according to the preceding claim, in which the ether derivative is selected from the group consisting of methyl ether, ethylether, propylether, butylether, hydroxymethylether, hydroxyethylether, hydroxypropylether, hydroxyethylmethylether and hydroxypropylmethylether and derivatives thereof.

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14. A composition according to claim 1, in which the derivative has an amylose content of up to about 95% by weight with respect to that of the starch.

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15. A composition according to the preceding claim, in which the derivative has an amylose content of up to about 85% by weight with respect to that of the starch.

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16. A composition according to the preceding claim, in which the derivative has an amylose content of up to about 75% by weight with respect to that of the starch.

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17. A composition according to the preceding claim, in which the derivative has an amylose content of up to about 65% by weight with respect to that of the starch.

18. A composition according to the preceding claim, in

- 33 -

which the derivative has an amylose content of up to about 45% by weight with respect to that of the starch.

- 5 19. A composition according to the preceding claim, in which the derivative has an amylose content of between about 30 and about 35% by weight with respect to that of the starch.
- 10 20. A composition according to claim 14, in which the derivative has an amylose content of between about 10 and about 15% by weight with respect to that of the starch.
- 15 21. A composition according to claim 1, wherein the starch derivative has an equilibrium moisture content of less than about 7% at 25°C and a relative humidity of about 50%.
- 20 22. A composition according to the preceding claim, wherein the starch derivative has an equilibrium moisture content of less than about 5% at 25°C and a relative humidity of about 50%.
- 25 23. A composition according to claim 1, wherein the starch derivative has an equilibrium moisture content of less than about 2% at 25°C and a relative humidity of about 50%.
- 30 24. A composition according to claim 1, in which the at least one member is present in the composition at a concentration of from 10 to 200 parts per 100 parts of dry starch.
- 35 25. A composition according to claim 1, in which the at least one member is present in the composition at a concentration of from 10 to 120 parts per 100 parts of dry starch.
26. A composition according to claim 1, in which the

- 34 -

composition comprises from about 10 to about 100 parts of said polymer per 100 parts of starch.

5 27. A composition according to claim 1, in which the composition comprises from about 10 to about 85 parts of said polymer per 100 parts of starch.

10 28. A composition according to claim 1, in which the composition comprises from about 20 to about 40 parts of said polymer per 100 parts of starch.

15 29. A composition according to claim 1, in which the alkenol homopolymer is polyvinyl alcohol.

30. A composition according to claim 29, in which the polyvinyl alcohol is substantially completely hydrolysed.

20 31. A composition according to claim 29, in which the polyvinyl alcohol is hydrolysed to an extent of from about 75 to about 100%.

25 32. A composition according to claim 29, in which the polyvinyl alcohol is hydrolysed to an extent of from about 85 to about 99%.

30 33. A composition according to claim 29, in which the polyvinyl alcohol is hydrolysed to an extent of from about 87 to about 99.9%.

34. A composition according to claim 29, in which the polyvinyl alcohol has a number average molecular weight of from 15,000 to 250,000.

35 35. A composition according to claim 34, in which the polyvinyl alcohol has a number average molecular weight of from 15,000 to 150,000.

36. A composition according to claim 35, in which the

- 35 -

polyvinyl alcohol has a number average molecular weight of from 160,000 to 250,000.

- 5 37. A composition according to claim 1, in which the polyvinyl alcohol has a degree of hydrolysis of at least about 97% and has a number average molecular weight of from about 15,000 to about 150,000.
- 10 38. A composition according to claim 36, in which the polyvinyl alcohol has a degree of hydrolysis of at least about 97% and has a number average molecular weight of from about 50,000 to about 150,000.
- 15 39. A composition according to claim 36, in which the polyvinyl alcohol has a degree of hydrolysis of at least about 97% and has a number average molecular weight of from about 70,000 to about 150,000.
- 20 40. A composition according to claim 36, in which the polyvinyl alcohol has a degree of hydrolysis of at least about 97% and has a number average molecular weight of from about 100,000 to about 150,000.
- 25 41. A composition according to claim 1, in which the alkenol homopolymer or copolymer is a pre-treated polyvinyl alcohol which has been obtained from a melt of polyvinyl alcohol which has been formed by adding  
30 sufficient energy to the polyvinyl alcohol to both melt it and substantially eliminate crystallinity in the melt, whilst simultaneously removing energy from the polyvinyl alcohol melt at a rate sufficient to avoid its decomposition.
- 35 42. A composition according to claim 41, in which the polyvinyl alcohol further comprises sodium acetate and phosphoric acid in a molar ratio of about 2 to 1.
43. A composition according to claim 42, in which the pre-treated polyvinyl alcohol has a maximum melt

- 36 -

temperature, as determined by differential scanning calorimetry, which is at least about 5°C lower than that of the corresponding untreated polyvinyl alcohol.

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44. A composition according to claim 1, further comprising an alkenol copolymer containing vinyl alcohol units and aliphatic chain units as obtained by co-polymerization of vinyl acetate with ethylene and/or propylene with subsequent hydrolysis of the vinyl acetate groups.

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45. A composition according to the preceding claim, in which the copolymer comprises ethylene/vinyl alcohol.

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46. A composition according to claim 44, in which the molar ratio of vinyl alcohol units to alkylene units is from about 40:60 to about 90:10.

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47. A composition according to the preceding claim, in said molar ratio is from about 45:55 to about 70:30.

48. A composition according to claim 47, in which the ethylene vinyl alcohol has an ethylene content of 44%.

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49. A composition according to claim 1, in which the composition further includes at least one member selected from the group consisting of extenders, fillers, lubricants, mould release agents, plasticisers, stabilisers, coloring agents flame retardants, alkali or alkaline earth metal salts, and boron-containing compounds.

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50. A composition according to claim 1, in which the composition further contains in an amount up to 60 %, by weight of the total composition, one or more hydrophobic thermoplastic polymers selected from the group consisting of polyolefines, polyisobutylenes, polypropylenes, vinylpolymers polystyrenes; polyacrylonitriles (PAN);

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- 37 -

polyvinylcarbazoles (PVK); substantially water-insoluble poly(acrylic acid) esters or poly(methacrylic acid) esters; polyacetals (POM); polycondensates thermoplastic  
5 polyesters, polycarbonates, polyurethanes, poly(alkylene terephthalates); polyarylethers; thermoplastic polyimides; poly(hydroxybutyrate) (PHB) and high molar-mass, substantially water-insoluble poly(alkylene  
10 oxides); ethylene/vinyl acetate-copolymers (EVA); ethylene/vinyl alcohol-copolymers (EVOH); ethylene/acrylic acid-copolymers (EAA); ethylene/ethyl acrylate-copolymers (EEA); ethylene/methyl  
15 acrylate-copolymers (EMA); ABS - copolymers; styrene/acrylonitrile-copolymers (SAN); and mixtures thereof.

51. A composition according to claim 49, in which said fillers are present in said composition at a  
20 concentration of up to about 20% by weight, based on the weight of the composition.

52. A composition according to claim 49, in which said plasticisers are present in said composition at a  
25 concentration of between about 0.5% and about 15% by weight, based on the weight of the composition.

53. A composition according to claim 52, in which said plasticisers are present in said composition at a  
30 concentration of between about 0.5% and about 5% by weight, based on the weight of the composition.

54. A composition according to claim 49, in which the sum of the plasticizer and water content of said  
35 composition does not exceed about 25% by weight, based on the weight of the composition.

55. A composition according to the preceding claim, in which the sum of the plasticizer and water content of said composition does not exceed about 20% by weight, based on the weight of the composition.

- 38 -

56. A composition according to claim 49, in which said coloring agents are present in said composition at a concentration of between about 0.01 and about 10% by weight, based on the weight of the composition.

57. A composition according to claim 49, in which said lubricants are selected from the group consisting of mono or diglycerides, lecithin and stearic acid.

58. A composition according to claim 57, in which the lubricant is stearic acid.

59. A composition according to the previous claim, in which the lubricant is present in the composition at a concentration of up to 10 parts per 100 parts of starch.

60. A composition according to the previous claim, in which the lubricant is present at a concentration of between 1 and 3 parts per 100 parts of starch.

61. A composition according to claim 59, in which the lubricant is present in the composition at a concentration of 1 part per 100 parts of starch.

62. A composition according to claim 1, in which the composition comprises a nucleating agent, having a particle size of from about 0.01 to about 5 microns, selected from the group consisting of silica, titania, alumina, barium oxide, magnesium oxide, sodium chloride, potassium bromide, magnesium phosphate, barium sulphate, aluminum sulphate, boron nitrate and magnesium silicate, or mixtures thereof.

63. A composition according to the previous claim, in which the nucleating agent is magnesium silicate (micro talcum).

64. A composition according to claim 62, in which the



- 39 -

composition comprises up to 10 parts of agent per 100 parts of starch.

5 65. A composition according to claim 64, in which the composition comprises from 1 to 3 parts of said agent per 100 parts of starch.

10 66. A composition according to claim 65, in which the composition comprises 2 parts of said agent per 100 parts of starch.

67. A composition according to claim 49, in which the  
15 flame retardant is selected from the group consisting of guanidinium phosphate; diethyl-N,N-bis(2-hydroxyethyl) aminomethyl phosphonate; dimethyl methylphosphonate; phosphonic acid, methyl-, dimethylester, polymer with oxirane and phosphorous oxide; aliphatic  
20 phosphate/phosphonate oligomers; tributyl phosphate; triphenyl phosphate; tricresyl phosphate; 2-ethylhexyl diphenyl phosphate; and tributoxyethyl phosphate; bis (hydroxypropyl) sec.butyl phosphine oxide; polypropoxylated dibutyl pyrophosphoric acid; a mixture  
25 of phosphonic acid, methyl-, (5-ethyl-2-methyl-1,3,2-dioxaphosphorinan-5-yl)methyl ethyl ester, P-oxide and phosphonic acid, methyl-, bis [(5-ethyl-2-methyl-1,3,2-dioxaphosphorinan-5-yl)methyl] ester,  
30 P,P'-dioxide as sold under the trade name Amgard V19; ammonium polyphosphate; ethylenediamine polyphosphate; melamine phosphate; dimelamine phosphate; and microencapsulated red phosphorous.

35 68. A composition according to claim 67, wherein the flame retardant is ammonium polyphosphate or ethylenediamine polyphosphate or a mixture thereof.

69. A composition according to claim 67, wherein the ammonium polyphosphate or ethylenediamine polyphosphate

- 40 -

are buffered with disodium orthophosphate.

5 70. A composition according to claim 49, wherein the flame retardant is selected from the group consisting of guanidinium sulfate; ammonium sulfate; ammonium sulfamate; and tetrakis (hydroxymethyl) phosphonium sulfate.

10 71. A composition according to claim 49, wherein the flame retardant is present in the composition in an amount of from about 0.1 to about 10%, by weight with respect to that of the starch component of the composition.

15 72. A composition according to claim 70, wherein the flame retardant is present in the composition in an amount of from about 1 to about 6%, by weight with respect to that of the starch component of the composition.

20 73. A composition according to claim 72, wherein the flame retardant is present in the composition in an amount of from about 2 to about 4% by weight with respect to that of the starch component of the composition.

25 74. A composition according to claim 49, in which the boron containing compounds are selected from the group consisting of boric acid, metaboric acid, alkali and alkaline earth metal salts, borax and derivatives thereof.

30 75. A composition according to claim 74, in which said compounds are present in the composition in an amount of between 0.002 and 0.4%, by weight with respect to that of the composition.

76. A composition according to claim 75, in which said compounds are present in the composition in an amount of

- 41 -

between 0.01 and 0.3%, by weight with respect to that of the composition.

5 77. A composition according to claim 49, in which the inorganic salts of alkali or alkaline earth metals are present in an amount of from 0.1 to 5% by weight with respect to that of the composition, and are selected from the group consisting of LiCl and NaCl.

10

78. A composition according to claim 1, in which the starch is  
at least one member selected from the group consisting of chemically modified starches of vegetable origin, which  
15 starches are derived from potatoes, rice, tapioca, corn, pea, rye, oats, wheat, including physically modified starch, irradiated starch, starch in which mono-valent and di-valent ions associated with phosphate groups therein have been removed, either partly or wholly, and  
20 optionally replaced, either partly or wholly, by different divalent ions or with mono or polyvalent ions; pre-extruded starches and starches which have been so heated as to undergo the specific endothermic transition characteristically preceding oxidative and thermal  
25 degradation.

79. A composition according to any preceding claim, which is in the form of a member selected from the group  
30 consisting of a melt, foam, film, granulate, pellet, and powder.

80. A composition according to claim 79, which is in the form of a foam.

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81. A composition according to claim 80, in which the bulk density of the composition is in the range of about 8.5 to about 30kg/m<sup>3</sup>.

82. A composition according to claim 80, in which the resiliency

- 42 -

of the composition is in the range of about 46 to 63%.

83. A composition according to claim 80, in which the  
5 compressibility of the composition is in the range of  
about 6 to 15%.

84. A composition according to claim 79, in the form of  
a melt.  
10

85. A composition according to claim 79, when used in  
the manufacture of shaped articles including bottles,  
films, pipes, rods, laminated films, sacks, bags,  
15 granules, powders, pellets, foams, containers, cartons,  
trays, cups, dishes, sheets, packaging materials, and  
foamed packaging materials -including loose fill.

86. A composition according to claim 1, when shaped by a  
20 process selected from the group consisting of foaming,  
filming, compression molding, injection molding, blow  
molding, vacuum forming, thermoforming, extrusion,  
coextrusion, and combinations thereof.

87. A composition according to claim 1, when shaped by a  
25 foaming process.

88. A composition according to claim 1, when shaped by a  
filming process.

89. A composition according to claim 1, when injection  
30 molded.

90. A composition according to claim 1, when extruded or  
35 co-extruded.

91. A composition according to claim 1, when shaped by a  
process selected from the group consisting of compression  
molding, blow molding, vacuum forming, thermoforming,  
and combinations thereof.

- 43 -

92. A method for producing the composition of claim 1, characterized by:

- 5 a) providing a starting composition comprising a starch derivative, a plasticizer and at least one member selected from alkenol homopolymers and/or alkenol copolymers;
- 10 b) adjusting the plasticizer content of the composition to between about 0.5 and about 40% by weight of the total composition during processing or plastification;
- 15 c) heating the thereby adjusted composition in a closed volume at a temperature of between 100 and 220°C and at a pressure corresponding at least to the moisture vapor pressure at said temperature for a time at least sufficient to form a melt of the composition;
- 20 d) removing any excess moisture before the extruder die to obtain a moisture content of between about 5% and about 20%;  
and -
- 25 e) extruding the thereby heated composition.

93. The method of the preceding claim, in which the plasticizer is water.

- 30 94. The method of the preceding claim, wherein the plasticizer content in step b) is adjusted to between about 15 and about 40% by weight of the total composition, in which the obtained moisture content in step d) is between about 10% and about 20%, and in which  
35 the heated composition optionally is extruded under conditions whereby the extrudate assumes a cross section greater than that of the exit orifice of the extruder die.

95. The method of claim 92, in which the said at least one member comprises polyvinyl alcohol.

- 44 -

96. The method of the preceding claim, in which the alkenol homopolymer and/or copolymer is a pre-treated polyvinyl alcohol which has been obtained from a melt  
5 which has been formed by adding sufficient energy to the polyvinyl alcohol to both melt it and substantially eliminate crystallinity in the melt, whilst simultaneously removing energy from the polyvinyl alcohol melt at a rate sufficient to avoid its decomposition.

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97. The method of the preceding claim, in which the composition further comprises sodium acetate and phosphoric acid in the molar ratio of about 1 to 2.

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98. The method of claim 96, in which the pre-treated polyvinyl alcohol has a maximum melt temperature, as determined by differential scanning calorimetry, which is at least about 5°C lower than that of the corresponding untreated polyvinyl alcohol.

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99. The method of claim 96, in which at least about 0.27kWh/kg of specific energy is added to the polyvinyl alcohol during pre-treatment both to melt it and  
25 substantially eliminate crystallinity in the melt.

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100. The method according to the preceding claim, in which the amount of specific energy is about 0.3 to 0.6kWh/kg.

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101. The method of claim 93, in which, prior to extrusion, the moisture content of the composition is adjusted to from 10 to 20% by weight of the total composition and in which the composition is heated at a  
35 temperature of from 100 to 200°C, and at a pressure corresponding at least to the moisture vapor pressure at said temperature for a time of from 0.5 to 2 minutes.

102. The method of claim 93, in which, prior to extrusion, the moisture content of the composition is adjusted to from 15 to 18% by weight of the total

- 45 -

composition and in which the composition is heated at a temperature of from 150 to 200°C and at a pressure corresponding at least to the moisture vapor pressure at said temperature for a time of from 0.5 to 1 minute.

103. The method of claim 94, in which, prior to extrusion, the moisture content of the composition is adjusted to 17% by weight of the total composition and in which the composition is heated at a temperature of from 180 to 200°C and at a pressure corresponding at least to the moisture vapor pressure at said temperature for a time of from 0.5 to 1 minute.

104. The method according to claim 102, in which the composition is heated to a temperature above the melting and glass transition temperature of the starch material.

105. The method of claim 93, wherein the starting composition optionally consists at least of the combination of starch and one member selected from alkenol homopolymers and copolymers which have been pre-combined under conditions sufficient to have formed a melt.

106. The method of the preceding claim, wherein the starting composition has been melted in the presence of from 15 to 40% moisture, by weight of the composition.

107. The method according to the preceding claim, wherein the starting composition has been melted at a temperature of from 100 to 200°C.

108. A method of shaping the composition of claim 1, selected from the group consisting of foaming, filming, compression molding, injection molding, blow molding, vacuum forming, thermoforming, extrusion, coextrusion, and combinations thereof.

- 46 -

109. A method of shaping the composition of claim 84,  
selected from the group consisting of foaming, filming,  
compression molding, injection molding, blow molding,  
5 vacuum forming, thermoforming, extrusion, coextrusion,  
and combinations thereof.

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# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 92/02003

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl.5                      C 08 L    3/00    //(C 08 L    3/00                      C 08 L    29:04 )		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl.5	C 08 L	
Documentation Searched other than Minimum Documentation to the extent that such documents are included in the fields searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
Y	WO,A,9102023 (BASTIOLI et al.) 21 February 1991, see page 2, line 8 - page 4, line 2; page 5, lines 18-20; page 6, line 9 - page 7, line 11; example 2, claims 1-5,7,8,11,13	1,24-29 ,41-47, 49-51, 62,78- 80,84- 87,89, 92-100, 108-109
Y	--- EP,A,0415357 (AIR PRODUCTS AND CHEMICALS) 6 March 1991, see page 4, lines 12-40; page 5, lines 7-20,42-49; page 7, lines 53-55; claims (cited in the application)	1,24-29 ,41-47, 49-51, 62,78- 80,84- 87,89,
-/-		
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><sup>10</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p> </div> </div>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
10-07-1992		27. 08. 92
International Searching Authority		Signature of Authorized Officer
EUROPEAN PATENT OFFICE		J.-F. MAZET

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		Relevant to Claim No.
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	
	---	92-100, 108-109
X	EP,A,0400532 (BUTTERFLY) 5 December 1990, see the whole document	1-3,6, 24-28, 44-50, 78,79, 84-86, 88-91, 108 109
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X	EP,A,0374993 (AMYLUM) 27 June 1990, see page 2, line 36 - page 3, line 36; page 4, lines 1-40; page 7, line 52 - page 8, line 18	1,2,24- 33,78, 79,84- 86,88, 92,93, 95,108
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X	EP,A,0376201 (NATIONAL STARCH AND CHEMICAL CORP.) 4 July 1990, see page 3, lines 5-50; page 4, line 1 - page 5, line 9; page 4, line 31 - page 6, line 4; examples III,VI,VII; claims (cited in the application)	1-3,12- 18,24- 29,49- 51,70, 77-95, 108,109
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**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
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US 9202003

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